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On the possible formation of H^- by way of H_2^-

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In a recent discussion of certain dark structures in the solar corona Öhman [1] has suggested that these structures may be explained as absorption structures, originating from H^- ions. According to Öhman one possibility for the formation of these ions would be by collisions between electrons and H_2 molecules in the ground state, followed by capture of the electrons in formation of H_2^- ions with subsequent dissociation of H_2^- into H and H^-. This reaction can be written as follows:

$$H_2(X\,^1\Sigma_g^+) + e \rightarrow H_2^-\,(^2\Sigma_u^+) \rightarrow H\,(^2S) + H^-\,(^1S). \tag{1}$$

Now, as a matter of fact, Öhman shows that even under the most favourable conditions the reaction (1) alone cannot explain the great heights of dark structures like those observed sometimes in white light in prominence regions and in the polar streamers of the solar corona. However, without going into any details, Öhman suggests that these structures of great heights could be explained by a recombination of H_2 by an inverse predissociation.

The present author would like to propose the following reaction formula for this inverse predissociation:

$$H\,(^2S) + H\,(^2P) \rightarrow H_2\,(f\,^3\Sigma_u^+) \xrightarrow[\text{conversion}]{\text{internal}} H_2\,(d\,^3\Pi_u). \tag{2}$$

This reaction should be fairly probable in the solar corona, where the populations of the excited states of H are comparatively large. After the step (2) the reaction can follow the different paths (3), (4) or (5) below, the latter being continued in (6), (7), (8), (9) or (10):

$$\begin{tikzcd}
 & H_2^-\,(^4\Pi_u) \arrow[r] & H\,(^2S) + H^-\,(^3P), & (3) \\
H_2\,(d\,^3\Pi_u) + e \arrow[ur] \arrow[dr] & & & \\
 & H_2^-\,(^2\Pi_u) \arrow[r] & H\,(^2S) + H^-\,(^3P), & (4)
\end{tikzcd}$$

$$H_2\,(d\,^3\Pi_u) \xrightarrow{\text{radiation}} H_2\,(a\,^3\Sigma_g^+), \tag{5}$$

$$\begin{tikzcd}
 & H_2^-\,(^4\Sigma_u^+) \arrow[r] & H\,(^2S) + H^-\,(^3S), & & (6) \\
H_2\,(a\,^3\Sigma_g^+) + e \arrow[ur] \arrow[dr] & & & & \\
 & H_2^-\,(^2\Sigma_g^+) \arrow[r] \arrow[dr, "\text{radi-}\atop\text{ation}"'] & H\,(^2S) + H^-\,(^1S), & & (7) \\
 & & H_2^-\,(^2\Sigma_u^+) \arrow[r] \arrow[dr] & H\,(^2S) + H^-\,(^1S), & (8) \\
 & & & H_2\,(X\,^1\Sigma_g^+) + e, & (9)
\end{tikzcd}$$

$$H_2\,(a^3\Sigma_g^+)\xrightarrow{\text{radiation}}H_2\,(b^3\Sigma_u^+)\rightarrow H\,(^2S)+H\,(^2S). \qquad (10)$$

This scheme is by no means exhaustive but is likely to include the most important possibilities.

Now, the existence of H_2^- has never been proved experimentally. Moreover, the only previous theoretical investigation of this ion was concerned solely with the lowest state $^2\Sigma_u^+$. This investigation was a quantum mechanical valence bond treatment with two variation parameters, carried out by Eyring *et al.* [2]. They found the ground state of H_2^- to be stable, having a dissociation energy of 37.4 kcal/mole.

The present investigation aims at a more detailed study of the reactions (1)–(10) and an estimate of the transition probabilities. For this purpose the potential curves of the ground state and the lowest excited states of H_2^- have been studied theoretically by means of a valence bond treatment, involving 3–6 variation parameters. According to the preliminary results of this more accurate computation the ground state $^2\Sigma_u^+$ is found to be stable in agreement with the previous calculation [2], although the value of the dissociation energy comes out considerably smaller. The preliminary results also indicate that all the excited states except $^4\Sigma_u^+$ should be unstable. Moreover, other excited states of H_2^- than those involved in the reactions (3)–(9) seem to be much higher excited and will thus lead to less probable reactions. The details of all the potential curves will be published later, when some of the integrals involved have been recalculated with greater accuracy by aid of an electronic computor.

The reactions of special interest for the present problem are those giving H^- as a final product. Of these reactions (2) → (3), (2) → (4) and (2) → (5) → (6) give H^- in excited states. These states are very probably unstable, according to discussions by other authors [3] and according to the present computational results. Consequently, these states will dissociate into $H+e$. However, the two reactions (2) → (5) → (7) and (2) → (5) → (8) give the stable $H^-\,(^1S)$ as a final product. There are thus at least two other reactions than (1), which lead to the formation of H^- in the stable ground state. This seems to give a possibility of verifying Öhman's tentative explanation of the dark structures of considerable heights.

It should also be noted that the reaction (2) → (5) → (9) indicates a possible reaction path for the formation of H_2 in the ground state by two-body collisions of hydrogen atoms.

The discussion of transition probabilities in the reactions, mentioned above, will be postponed until the final publication.

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3. See e. g. H. S. W. Massey, Negative Ions, Cambridge 1950, p. 20.

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